Letters to the Editor

Indian J. Phys. **49**, 155–157 (1975)

Variation of viscosity with temperature in some molten electrolytes

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(*Received* 18 *May* 1974, *revised* 9 *September* 1974)

Eyring & Hirschfelder (1937) and Ewall & Eyring (1937) considered the flow of a liquid as a rate process, in so far as it takes place with a definite velocity under given conditions and applied the theory of absolute reaction rates to the problem of viscosity and derived an exponential equation,

$$\eta = A \exp[E_{vis}/RT], \tag{1}$$

where E_{vis} is the energy of activation for viscous flow.

The above equation, although meant for pure non-associated liquids, has been found to hold good in the case of a number of aqueous solutions by Berl, Umstatter & Karrel (1931) and by Joshi & Solanki (1940). Ram Gopal (1953) applied the above equation to a few cases of supersaturated aqueous solutions with some success.

Here the applicability of the above equation to the case of molten salts of LiCl, NaCl, KCl, CsCl and $HgBr_2$ has been examined. Recently Suryanarayana (1972) showed the thermodynamic significance of internal pressure and its role in transport processes. Hence from the available data the cohesive energy of the solutions (product of internal pressure and molar volume) has also been calculated and comparison has been made with E_{vis} values obtained from the slopes of $\log \eta$ versus $1/T$ plots, (figure 1), for the first four electrolytes.

Data of viscosity of molten salts of LiCl, NaCl, KCl and CsCl have been obtained from literature (Janz 1967). Incidentally from the same source of data analogous to the well-known Trouton's constant, the ratio of cohesive energy of the solutions to the temperature at their respective melting points was examined for LiCl, NaCl, KCl, CsCl, NaBr, KBr, NaI, KI and CsBr. Cohesive energy of these molten salts was obtained from the product of the molar volume at the concerned temperature and the internal pressure. Internal pressure was computed as given by Suryanarayana (1972) making use of the equation :

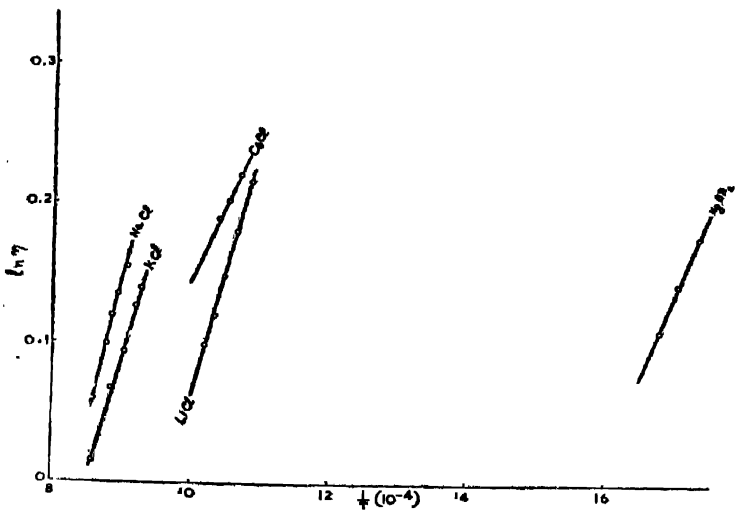

Fig. 1. ln η *Vs* $1/T$ for molten Salts

Internal pressure, $$\pi = \frac{T\alpha}{\beta_T}, \qquad \ldots (2)$$

wherein α is the thermal coefficient and β_T is the isothermal compressibility. In cases where the isothermal compressibility was available in a range of temperatures, the value at a given temperature as for example at the melting point was obtained by extrapolation as the temperature variation of isothermal compressibility was linear in all the cases. Results obtained are presented in the table 1.

Table 1

Electrolyte	$R \times$ slope $= E_{vi}$ (in K Cal.)	π in Atm ($\times 10^8$)	πV (in K cal)	$\pi V/T$ ($\times 10^8$)	$\Delta G_{vi}^{\neq}$ (in K Cal)
LiCl	16.52	135.5	9.135	4.342	16.76
NaCl	17.84	130.5	11.650	4.560	20.42
KCl	14.43	112.5	13.050	5.264	19.84
CsCl	10.18	96.92	13.900	6.351	18.42
NaBr	...	117.4	12.330	5.076	...
KBr	...	113.7	14.030	6.295	...
NaI	...	88.24	11.470	5.164	
KI	...	76.03	12.330	5.420	...
CsBr	...	73.60	11.920	5.505	...
$HgBr_2$	9.456	...	...	...	...

From the results it is clear that in the case of the five molten salts examined, eq. (1) is applicable. Suryanarayana & Venkatesan (1958) showed for the first time that the variation of viscosity with temperature of highly concentrated aqueous solutions of strong electrolytes like NaCl, KCl, $NaNO_3$ and KNO_3 follows eq. (1) upto the limit of saturation. Our observation extends the limit of applicability of eq. (1) to molten salts.

Column (2) in the table shows the E_{vis} values from available data for the four electrolytes examined. Glasstone *et al* (1941) gave a relation between the free energy of activation for flow and energy of vaporisation. By extrapolating the available viscosity data upto the melting temperature in each case of the first four electrolytes, we have calculated $\Delta G_{vis}^{\neq}$ using Eyring's equation (Glasstone *et al* 1941). The values are tabulated in the last column of the table. Suryanarayana (1972) showed that in a transport process like viscosity the free energy for viscous flow is almost equal to πV.

From the available data πV has been calculated at the melting point and tabulated in column (4) of the table. The πV values given for the first four electrolytes are comparable to the $\Delta G_{vis}^{\neq}$ values given in the last column though not identical. The correspondence between the values in column (4) and ΔG_{vis} values in the last column is fairly good. The order of the experimentally obtained E_{vis} values in column (2) is fairly in good agreement both with the πV values in column (4) and $\Delta G_{vis}^{\neq}$ values in the last column.

As πV corresponds to the energy of vaporisation, column (5) shows the quotient $\pi V/T$ analogous to Trouton's constant, namely, $\Delta H/T$ at the boiling point for various liquids. It is remarkable that the values lie between 4.3 and 6.3×10^8 showing a fair constancy for nine electrolytes at their melting points.

The authors thank Dr. C. V. Suryanarayana and Mr. J. Kuppusami for useful discussions and Dr. H. V. K. Udupa, Director, Central Electrochemical Research Institute for permission to use the library facilities of the Institute. They also thank Dr. Kulandaiswami, Director of Technical Education, Government of Tamil Nadu, Professor S. Srinivasan, Principal, A. C. College of Engineering & Technology and Mr. N. S. Rajagopalan, Head of the Department for their encouragement.

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